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54 Cementitious compositions for layered applications.

(57) The interlayer adhesion and final strength of cementitious compositions which are applied in consecutive layers are improved by the incorporation in the compositions of an admixture which is a combination of a waterproofing agent and a water retention agent. The invention is particularly applicable to sprayed concrete.

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This invention relates to cementitious compositions, more particularly to cementitious compositions for application to substrates in consecutive layers, and most particularly to those which are applied by spraying, and to admixtures for use therein.

It is often required that a cementitious composition be applied in consecutive layers. The best known of such applications is the spraying of cementitious compositions such as "shotcrete", wherein a number of individual layers is applied by means of a shotcreting gun. One of the problems frequently encountered in such applications is cracking and shrinkage of the composition and bonding failures at the layer interfaces. The solution to this problem has hitherto been the application to the sprayed composition of a curing agent, that is, a preparation which is sprayed on the surface and which forms a film thereon. Typical examples include hydrocarbons, fatty acid salts and emulsions of paraffins or microwaxes. Because of the water loss at the surface of sprayed cementitious compositions, this must be done within a very short time of spraying - usually within 15-20 minutes. Moreover, before a further layer can be added, the curing agent must be removed, otherwise it may prevent adequate bonding between adjacent layers of sprayed composition. Various relatively easily-removable curing agents have been made and marketed, but they still involve the time-consuming work of application and renewal.

It has now been discovered that certain admixtures can be added to cementitious compositions prior to layer application and that these compositions not only remove the necessity for the application and removal of curing agents, but they may also confer considerable property advantages on the compositions. The invention therefore provides an admixture for use in a cementitious composition, which comprises at least one concrete waterproofing agent and at least one water retention agent.

The invention further provides a fluid cementitious composition comprising an admixture as hereinbefore described.

The invention further provides a method of providing a solid mass of cementitious material by preparing a fluid cementitious composition as hereinabove described, placing it and causing it to harden.

The invention further provides a method for the application of a cementitious composition comprising the preparation and placement in consecutive layers of a composition as hereinabove described.

By "concrete waterproofing agent" is meant an agent of the type commonly used to render concrete waterproof. Such agents are well known to the art and are well described in, for example, "Chemical Admixtures for Concrete" by M.R. Nixon and N.P. Mallvaganan (2nd Ed. Spon, 1986) the contents whereof are incorporated herein by reference. Any of the typical examples described therein - microwaxes, stearates and other long chain fatty acids, etc. - may be used. Such materials are normally applied to surfaces of cementitious compositions, and it is a surprising feature of this invention that the incorporation of such a material into an admixture as hereinabove described confers such advantageous results. It is possible to use more than one such material in an admixture according to the invention.

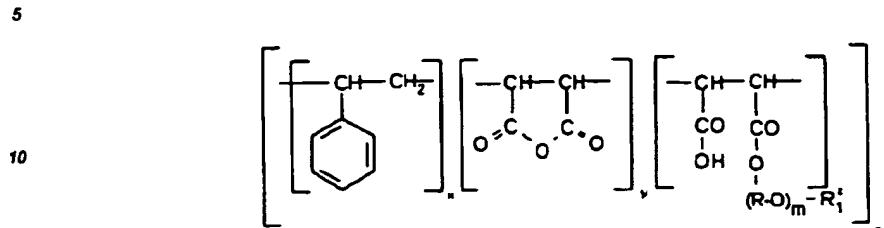
Particularly preferred materials are paraffin emulsions. By "paraffin emulsion" is meant an aqueous emulsion of a higher alkane having a fusion point above ambient temperature, which upon drying of the emulsion does not form a film in the sense that a paint forms a film (see also Römpf "Chemie Lexikon", 9th edition (Thieme Verlag 1989), volume 1, page 102, the contents of which are incorporated herein by reference). The emulsion may be stabilized by any convenient means, but it is preferable to use an anionically-emulsified paraffin mixture (fusion point of 45-51°C) with a particle size of less than 2μ. Examples of such paraffin emulsions are "Mobilcer" 55 or "Mulrex" 62 from Mobil and "Ubatol" FPG 860 from Cray Valley and "Tecol" BC 60/40 from Trüb Emulsion Chemie.

By "water retention agent" is meant a material which may be used to hold water within a cementitious composition or which promotes a better distribution of water throughout a cementitious composition. A group of preferred materials is that of the so-called "superabsorbent" materials. These materials, widely used in products such as diapers and incontinence pads, are readily available commercially (for example, the "Sanwei" (trade mark) materials) and are usually based on modified polysaccharides, for example acrylic-modified starch. However, the preferred water retention agent is a water-soluble poly(alkylene oxide) ("PAO") of molecular weight from 100,000-8,000,000. The requirement that the PAO be water-soluble means that it must include at least a high proportion of oxyethylene units; it is preferable that it be pure poly(ethylene oxide). It is also preferable that the PAO molecular weight lie in the range 2,000,000-5,000,000. Typical commercial products useful in the working of this invention may be found, for example, in the "Polyox" (trade mark) range of Union Carbide Chemicals and Plastics Company, Inc.

In a further embodiment of the invention, the admixture may additionally comprise a plasticizer or superplasticizer which is free from a β-naphthalene sulfonate-formaldehyde condensate ("BNS").

The plasticizer or superplasticizer useful in the present invention (and which may be used separate from or in any combination with the water retention and waterproofing agents) may be selected from the very wide range of such materials known to and used by the art, typical examples including lignosulfonates, hydroxycar-

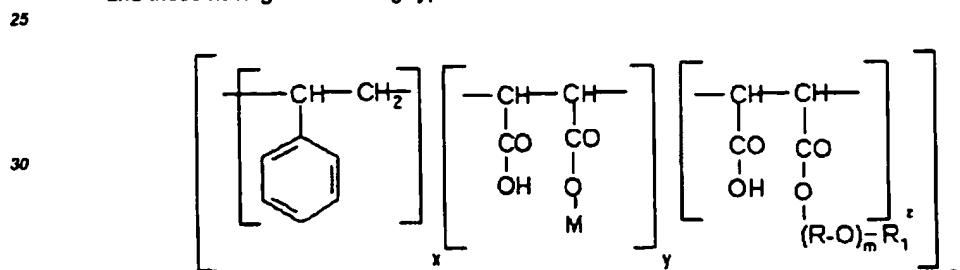
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boxylic acids, carbohydrates, melamine-formaldehyde condensates and styrene-maleic anhydride copolymers. The last-named are especially preferred, and the most preferred of these are styrene-maleic anhydride-derived copolymers in free acid or salt form and selected from the group consisting of those having the following types and numbers of monomer units:



in which R is an C_{2-6} -alkylene radical
 R_1 is a C_{1-20} -alkyl-, C_{6-9} -cycloalkyl- or phenyl group,
x, y and z are numbers from 0.01 to 100
m is a number from 1 to 100 and
n is a number from 10 to 100

20 with the provisos, that
i) the ratio of x to (y + z) is from 1:10 to 10:1 inclusive,
ii) the ratio of z:y is from 3:1 to 100:1 and
iii) $m + n = 15-100$

and those having the following types and numbers of monomer units:



in which M is hydrogen or the residue of a hydrophobic polyalkylene glycol or polysiloxane,
 R_1 , m and n are as hereinabove defined,
x, y and z are numbers from 1 to 100

with the provisos that
40 i) the ratio of x to (y + z) is from 1:10 to 10:1 inclusive,
ii) the ratio of z:y is from 5:1 to 100:1 and
iii) $m + n = 15-100$.

These copolymers (hereinafter "SMA") are described in United States Patent 5,158,916 and French Published Application 2 671 090 the contents whereof are incorporated herein by reference.

45 The waterproofing agent and the water retention agent may be added individually to a cementitious composition but they are preferably added combined. The invention therefore provides an admixture for a cementitious composition which is a physical blend of a concrete waterproofing agent as hereinabove described and a water retention agent as hereinabove described, optionally with a plasticizer or superplasticizer as hereinabove defined, either combined with or separate from the other admixture materials.

50 The admixture is easily prepared and a skilled person will readily comprehend how this can be done. For example, when the water retention agent is poly(alkylene oxide), the poly(alkylene oxide) is first dissolved in water to give a solution of about 1-3% solids by weight and the concrete waterproofing agent is blended with the solution.

55 The relative proportions of the waterproofing agent and the water retention agent used in the admixtures of the invention, both to each other and to cementitious compositions in which they are incorporated, depend largely on the natures of the waterproofing agent and the cementitious composition, the use to which the cementitious composition will be put, the method of application, the desired slump properties, and so on. The

skilled person can readily determine in each circumstance what are suitable proportions. As a general guide, the relative weight ratios of waterproofing agent to water retention agent are from 1:1 to 120:1, preferably from 20:1 to 25:1, and their combined presence is to the extent of from 0.5-5%, preferably of from 2.0-2.5% by weight solids on cement. When a plasticizer or superplasticizer is used, it is present in the proportion of from 0.01 to

5 10%, preferably from 0.1 to 3% by weight on cement. When a plasticizer or superplasticizer is present, the proportion of admixture preferably does not exceed 5% by weight on cement.

In use, the waterproofing agent and water retention agent are added to a cementitious composition prior to end-use, usually (and preferably) at the mixing stage. The water retention agent and the waterproofing agent may be added to the mix consecutively in any order or concurrently, or, preferably, they may be pre-blended to form a curing admixture as hereinabove defined and added in this form. Similarly, the plasticizer or superplasticizer, when present, may be added combined or separately, again preferably at the mixing stage.

The invention is applicable to any cementitious composition, but is especially useful to those which need to be applied in consecutive layers which must bond to each other, be it mortar, concrete or grout. It can be used with normal concrete, repair concrete or wet or dry spraying concrete, but it is especially applicable to wet spraying.

It has been found that cementitious compositions used in accordance with this invention, perform outstandingly well. Not only is there no longer a necessity to apply and remove curing agent, but also shrinkage and cracking are reduced (in some cases completely eliminated), and cement hydration, bonding between layers of cementitious composition and 28-day strength are all enhanced.

20 In addition to waterproofing agent, water retention agent and plasticizer or superplasticizer, other art-recognized admixtures may be added in known quantities. One particularly useful admixture is accelerator, used when the cementitious composition is to be sprayed.

The method of this invention may be used in conjunction with the method described in PCT Published Application WO 94/02428, the contents whereof are incorporated herein by reference to give a spraying cementitious composition of outstanding applicability and final properties. The invention therefore provides a process of applying a cementitious composition to a substrate, comprising the steps of

- a) preparing a cementitious composition which comprises an admixture as hereinabove described, which admixture comprises a styrene-maleic anhydride copolymer superplasticizer (preferably as hereinabove defined), and sufficient water to provide suitable fluidity;
- 30 b) conveying this composition to a point of application at which point there is added β -naphthalene sulfonate-formaldehyde condensate; and
- c) applying the composition to the substrate.

The amount of fluidity required and the achievement thereof will vary depending on the individual circumstances and requirements, but the skilled person will readily be able to achieve the necessary fluidity.

35 This process works especially well when the application method is spraying and BNS is added to the composition at a spray nozzle. The invention further provides a slump control system for a cementitious composition, comprising an admixture as hereinabove defined and BNS together with instructions for their use.

The combination of SMA and BNS is described in PCT Published Application WO 94/02428. It permits the regulation of the slump of a cementitious composition. Slump, as measured by ASTM C143, is the oldest and 40 most widely used measure of the workability of cementitious compositions. It has been found that a combination of SMA, BNS and concrete waterproofing agent gives good slump control. The performance is further enhanced by

- (a) the use the curing admixture as hereinabove defined, that is, by including a water retention agent as hereinabove defined, and
- 45 (b) the use with the BNS of known accelerators. Especially efficacious types of accelerators are aluminates and silicates, particularly sodium silicate ("water glass"). The above-mentioned copending application describes a preferred BNS/water glass combination which works well in this invention.

The invention is further described with reference to the following examples in which all parts are expressed by weight.

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Example

Use of the invention in shotcrete spraying.

A spraying concrete mix is prepared by mixing the following ingredients:

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	Portland cement	450 parts
5	microsilica	22 parts
	styrene-maleic anhydride copolymer ¹	6.75 parts
	PEO/paraffin blend ²	8 parts
10	sand (0-8mm)	1590 parts
	steel fibers (EE length 25-40 mm, diameter 0.5-0.6mm)	60 parts

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¹ As prepared in Example 1 of French Published Application 2 671 090

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² A 50/50 volume blend of "Tecol" BC 60/40 aqueous paraffin emulsion (ex Trüb Emulsions Chemie AG) and an aqueous poly(alkylene oxide) solution of the following constitution

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WSR-301 (ex Union Carbide)	1.0% by weight
MPEG-500 (ex Hoechst)	2.0% by weight
water	97.0% by weight

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This mixture is mixed, the order of mixing being, firstly, cement, microsilica sand and steel fibers, secondly styrene-maleic anhydride copolymer and finally the PEO/paraffin blend, and sufficient water is then added to give a water:cement ratio of 0.45. The slump of this mixture as measured by the method of ASTM C413 is 21cm. The mixture is sprayed on to a substrate through a spray nozzle, there being injected into the mixture at the nozzle a solution of the following constitution

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BNS sodium salt (40% aqueous solution)	3% by weight on solids
sodium silicate (36% solution)	30.6% by weight on solids
water	to 100%

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The injection rate is such that there is supplied 4% solution by weight of cement.

The sprayed concrete is allowed to harden and a further layer sprayed thereon.

For comparison, there is sprayed out the same composition with the following changes:

- (a) the PEO/paraffin blend is omitted and the sand content is raised 8 parts;
- (b) the 6.75 parts of SMA is replaced by 7.5 parts of BNS

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The same water:cement ratio (0.45) is used, giving a slump of just over 20 cm. When sprayed, there is injected 4% on cement of an aqueous solution of a commercially-available silicate activator.

Two sprayings are carried out, one being subsequently covered by a curing agent ("Protect Weiss" ex Master Builders Technologies, applied at a rate of 0.4 kg. solids/M²), the other being left uncured. A further layer is then applied to both, the curing agent being cleaned from that substrate which is coated thereon.

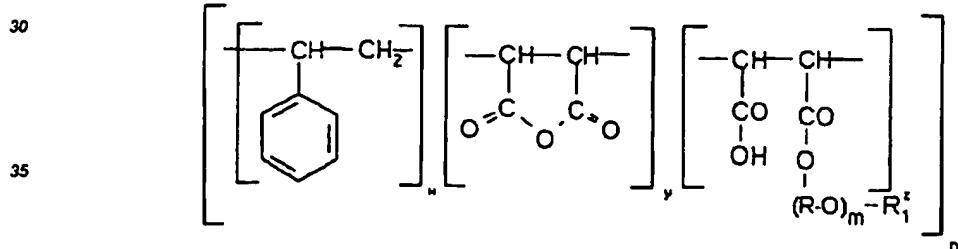
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The interlayer bonding, density and 28 day compressive strength are measured and the results are as follows:

	Bond strength (MPa)	Density	Compressive strength (MPa)	
5	Composition according to the invention	>2.0	2.33	41-43
10	Externally-cured composition	0.7-1.2	2.28	38-40
15	Uncured composition	<0.7	2.27	37

Claims

1. An admixture for use in curing cementitious composition, which comprises at least one concrete waterproofing agent and at least one water retention agent.
- 15 2. An admixture according to claim 1, wherein the water retention agent is a water-soluble poly(alkylene oxide) of molecular weight from 100,000 to 8,000,000.
- 20 3. An admixture according to claim 1 or claim 2, wherein the concrete waterproofing agent and the water retention agent are physically blended prior to use.
- 25 4. An admixture according to any one of claims 1-3, wherein the admixture additionally comprises a plasticizer or superplasticizer which is free from a β -naphthalene sulfonate-formaldehyde condensate.
5. An admixture according to claim 4, wherein the plasticizer or superplasticizer comprises at least one styrene-maleic anhydride-derived copolymer in free acid or salt form and having the following types and numbers of monomer units:

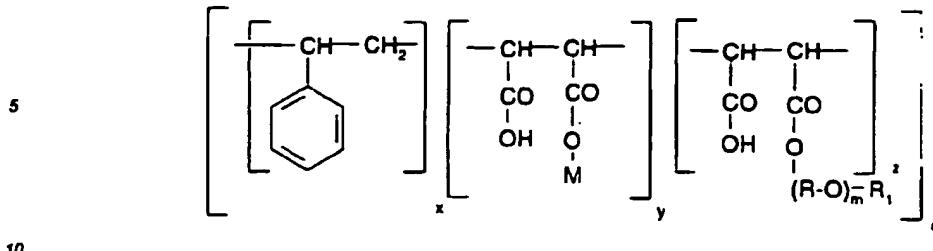


40 In which R is an C_{2-6} alkylene radical
 R_1 is a C_{1-20} alkyl-, C_{6-9} cycloalkyl- or phenyl group,
x, y and z are numbers from 0.01 to 100
m is a number from 1 to 100 and
n is a number from 10 to 100

45 with the provisos, that
i) the ratio of x to (y + z) is from 1:10 to 10:1 inclusive,
ii) the ratio of z:y is from 3:1 to 100:1 and
iii) m + n = 15-100 and those having the following types and numbers of monomer unit:

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in which M is hydrogen or the residue of a hydrophobic polyalkylene glycol or polysiloxane,
 R₁, m and n are as hereinabove defined

x, y and z are numbers from 1 to 100

15 with the proviso that

- i) the ratio of x to (y + z) is from 1:10 to 10:1 inclusive,
- ii) the ratio of z:y is from 5:1 to 100:1 and
- iii) m + n = 15-100.

- 20 6. A fluid cementitious composition, comprising an admixture according to any one of claims 1-5.
7. A method for the application of a cementitious composition comprising the preparation of a concrete mix and its placement in consecutive layers, characterized in that the composition comprises an admixture according to any one of claims 1-5.
- 25 8. A process of applying a cementitious composition to a substrate, comprising the steps of
 - a) preparing a cementitious composition which comprises an admixture according to claim 1, which admixture comprises a styrene-maleic anhydride copolymer superplasticizer, and sufficient water to provide suitable fluidity;
 - b) conveying this composition to a point of application at which point there is added β-naphthalene sulfonate-formaldehyde condensate; and
 - c) applying the composition to the substrate.
- 30 9. A method of providing a solid mass of cementitious material by preparing a fluid cementitious composition comprising an admixture according to any one of claims 1-5, placing it and causing it to harden.
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EUROPEAN SEARCH REPORT

Application Number
EP 94 81 0507

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
X	DE 31 05 576 A (HEINRICH ELSKES KG ET AL) 30 December 1982 * claims * ---	1,6	C04B28/02 //(C04B28/02, 24:02,24:22, 24:26,24:32, 24:42)
X	CHEMICAL ABSTRACTS, vol. 114, no. 26, 1 July 1991 Columbus, Ohio, US; abstract no. 252826, XP000194941 * abstract *	1	
Y	& JP 02 263 751 A (INAX CORP. ET AL) 26 October 1990 ---	2,3	
Y	CHEMICAL ABSTRACTS, vol. 103, no. 26, 30 December 1985 Columbus, Ohio, US; abstract no. 219928, XP000061248 * abstract * & JP 60 161 363 A (KAO CORP., JAPAN) 23 August 1985 ---	2,3	
X	EP 0 306 449 A (SANDOZ AG) 8 March 1989 * claims * ---	4,5	C04B
A	GB 2 164 930 A (IDEMITSU PETROCHEMICAL CO) 3 April 1986 ---	4-8	
P,A	DE 43 24 334 A (SANDOZ AG) 27 January 1994 * claims; examples *	1-8	
D	& WO 94 02428 A ---		
A	FR 2 659 078 A (ANHYSOL DIFFUSION) 6 September 1991 * claims 1-6 *	1-8	
D,A	FR 2 671 090 A (SANDOZ SA) 3 July 1992 * the whole document * ----	4,5	
The present search report has been drawn up for all claims:			
Place of search	Date of completion of the search	Examiner	
BERLIN	23 September 1997	Kuehne, H-C	
CATEGORY OF CITED DOCUMENTS			
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